

Modeling gas separation in metal-organic frameworks

Brad A. Wells · Alan L. Chaffee

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Abstract The gas adsorption and CO₂ separation properties of 9 different metal-organic frameworks (MOFs) have been modelled with grand canonical Monte Carlo (GCMC) adsorption simulations. Adsorption of both pure gases and gas mixtures has been studied. MOFs are shown to have high selectivity for polar gases such as CO₂ over non-polar gases such as N₂. Selectivity of one polar gas from another can be altered by changing the polarity of the framework, pore geometry and also temperature. Often features that lead to good selectivity of CO₂ from N₂ also lead to poor selectivity of CO₂ from H₂O.

Keywords Metal-organic framework · Carbon dioxide · Separation · Simulation

1 Introduction

Anthropogenic climate change is an important global challenge facing the future of humanity. Already the effects of global warming are becoming evident, with the last few years seeing the first climate refugees (Morton 2009; Wax 2007). While long term solutions in the form of renewable energy technologies are being developed, processes also need to be implemented to limit the amount of greenhouse gases, such as CO₂ that are released into the atmosphere.

These processes need to be both economic and efficient. Efficiency is especially critical since each process invariably involves an energy cost, which increases the amount of energy and therefore CO₂ that is being generated.

Carbon capture and storage (CCS) technologies are one promising way of reducing the amount of CO₂ released into the atmosphere from fossil fuel power generation. One of the central elements of this technology is separating and purifying CO₂ from the flue gas stream for later storage. Pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) are two gas separation processes that have been suggested for industrial scale capture of CO₂ from flue gases (Aaron and Tsouris 2005). In each of these processes a solid adsorbent acts as a selective CO₂ sponge, soaking up CO₂ in a higher pressure gas stream and then being regenerated by dropping the pressure. Several porous solids have been suggested for use in these processes, such as the zeolite 13X (Konduru et al. 2007). However a range of problems, such as high energy cost of regeneration limit the effectiveness of these more traditional adsorbents.

Metal-organic frameworks (MOFs) is another class of porous materials that have been suggested for use in a wide range of gas physisorption applications (Rosseinsky 2004). MOF structures consist of metal cations held together by anionic or neutral organic molecules. Covalent-organic frameworks (COFs) are analogous materials formed through the polymerization of boron containing organic molecules. Because of the wide range of possible cations and organic linkers MOFs and COFs of nearly any pore size and shape can be made. Indeed to date thousands of MOFs have been synthesized and detailed in the literature. Methods are also being developed, such as the reticular synthesis methods of Yaghi and co-workers (Yaghi et al. 2003) to rationally design and synthesize novel frameworks for specific applications.

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B.A. Wells · A.L. Chaffee (✉)
Cooperative Research Center for Greenhouse Gas Technologies,
School of Chemistry, Monash University, 3800, Australia
e-mail: alan.chaffee@sci.monash.edu.au

Unfortunately while thousands of MOFs are known, the CO₂ gas sorption and separation properties of only a small fraction of these have been recorded (Li et al. 2009). As a consequence of the difficulty of obtaining good gas sorption data molecular simulation is increasingly becoming an important tool in both screening a wide range of materials for potential uses and also understanding the mechanisms of gas adsorption (Keskin et al. 2009). For modeling equilibrium adsorption grand canonical Monte Carlo (GCMC) simulations (Frenkel and Smit 2002a, 2002b) is one of the most widely used techniques. Several studies have simulated the adsorption of pure CO₂ (Babarao and Jiang 2008, 2009; Liu et al. 2009b; Ramsahye et al. 2007a, 2007b; Yang and Zhong 2006a, 2008), as well as the separation of CO₂ from other gases (Babarao et al. 2009; Bae et al. 2008; Liu and Smit 2009a; Martin-Calvo et al. 2008; Yang and Zhong 2006a; Yang et al. 2007; Yazaydin et al. 2009) in MOFs. Of the separation studies only the one of the most recent ones by Snurr and co-workers (Yazaydin et al. 2009) considers the effect of water on CO₂ adsorption. This is important to their use as selective adsorbents of CO₂ from flue gas, as water is one of the important components of gases in both pre-combustion and post-combustion processes. As well as being adsorbed by MOFs, water has been shown to have detrimental effects to CO₂ adsorption. While small amounts of water can increase CO₂ adsorption (Yazaydin et al. 2009), and some MOFs such as Cu-MOF have been found to be overall stable in the presence of water (Cheng et al. 2009), moderate to large amounts of water has been shown to destroy the porosity and therefore the gas sorption properties of MOFs such as Cu₃(BTC)₂ (Liang et al. 2009), MOF-177 (Li and Yang 2007) and MOF-5 (Greathouse and Allendorf 2006). Because of the significance of water adsorption in these frameworks simulations of gas separation of flue gases should include water.

In this paper we present simulations of the gas adsorption and separation properties of 8 different MOF structures and 1 COF structure. The pure gas adsorption of gases relevant to flue gas separation in both pre and post combustion schemes, namely water, carbon dioxide, nitrogen and hydrogen has been calculated. The adsorption of gas mixtures representing typical gas streams in pre-combustion and post-combustion have also been simulated. From this data we are able to make several conclusions about the mechanism of gas adsorption in these frameworks, and how these mechanisms impact the selective adsorption of CO₂.

2 Computational methods

2.1 Framework structures

The general computational methodology employed here is similar to that used in our previous study (Wells et al. 2009),

but with some important modifications. As a starting point framework structures for each adsorbent have been taken from X-ray crystallography studies on each MOF already in the literature (Banerjee et al. 2008; Barthelet et al. 2002; Chae et al. 2004; Chui et al. 1999; Dybtsev et al. 2004; Klontzas et al. 2010; Li et al. 1999; Miller et al. 2009; Millward and Yaghi 2005). These structures were then optimized using density functional theory (DFT) calculations performed with the Siesta code (Jose et al. 2002). These calculations employed the PBE functional with an automatically generated double zeta basis set cut off at 5.0×10^{-3} Rydberg and pseudopotentials based on Abinit GGA pseudopotentials. The mesh cutoff was also set to 200 Rydberg. The resulting structures were then re-symmetrized to reflect the observed crystal symmetry. The final geometry of each structure is shown in Fig. 1.

2.2 Gas-framework potentials

The energy of each gas in the framework is given as the usual sum of dispersion/repulsion energies and electrostatic interactions. The dispersion/repulsion potential was modeled by the 9–6 Lennard Jones equation, which is given as

$$V(r_{ij}) = \varepsilon_{ij} \left[2 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^9 - 3 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

The pair parameters ε_{ij} and σ_{ij} are derived from single atom parameters using the 6th power combination rules

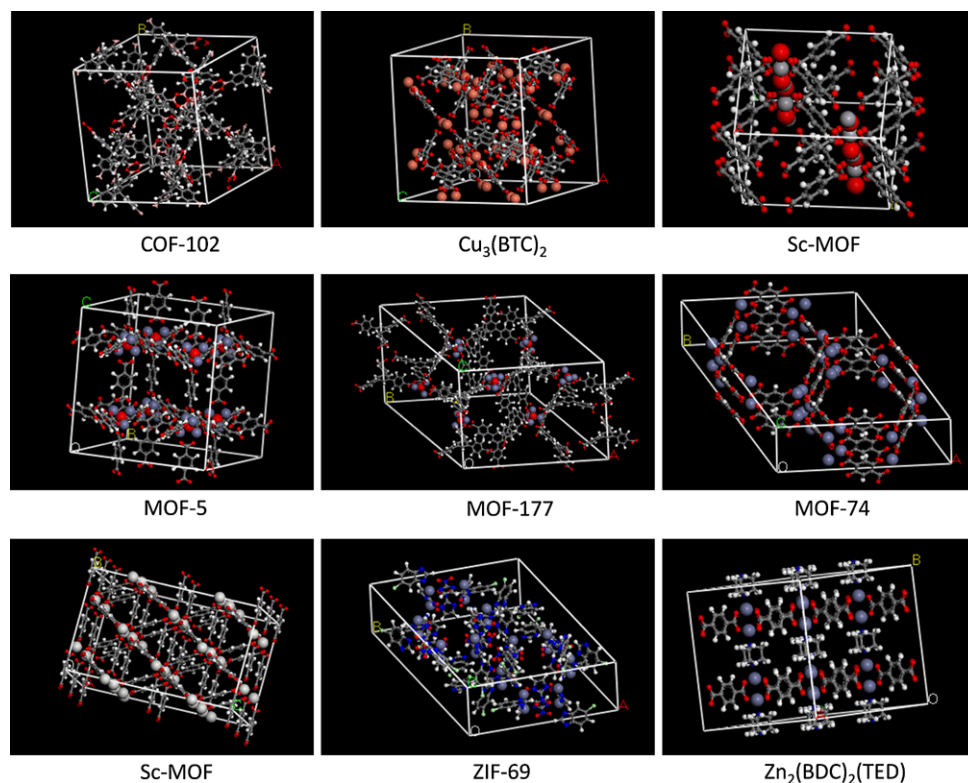
$$\sigma_{ij} = \left(\frac{\sigma_i^6 + \sigma_j^6}{2} \right)^{1/6}$$

and

$$\varepsilon_{ij} = \frac{2\sqrt{\varepsilon_i \varepsilon_j} (\sigma_i^3 \sigma_j^3)}{(\sigma_i^6 + \sigma_j^6)}$$

The single atom parameters were taken from the Compass forcefield (Sun 1998), with parameters being assigned by atomic type. Additional parameters for scandium ions and boron atoms, both of which are not parameterized in the Compass forcefield were taken from the Universal (Rappe et al. 2002) and Drieding (Mayo et al. 2002) forcefields respectively. The Lennard-Jones potential used a cutoff of 18.5 Å, with the potential being brought to zero over the last angstrom with a cubic spline function. To speed the calculation the interaction potential between each of the gas atoms and the framework atoms was calculated on a grid in the unit cell of each material, allowing values to be interpolated from the grid. To achieve the necessary accuracy a grid spacing of 0.1 Å was used.

Likewise the electrostatic interactions were calculated on a grid and interpolated during the calculation. In this

Fig. 1 Optimized structures of MOF and COFs in simulation

case however the electrostatic potential of each framework was calculated in a single-point calculation in Siesta. These calculations were the same as the geometry optimization calculations except that polarization functions were added to the basis set and the integration grid spacing was increased to 400 Rydbergs. This produces a grid spacing of less than 0.1 Å. To account for the differences between diffuse charges on the framework and point charges on the gas molecules a scaling factor of 1.5 was applied to all DFT calculated electrostatic fields. This method has been demonstrated previously to accurately model CO₂ adsorption in MOFs (Wells and Chaffee, in preparation).

2.3 Gas-gas interactions

The geometry of each of the gases was determined using geometry optimizations with the Compass molecular mechanics forcefield. Partial atomic charges on CO₂ and H₂O were assigned to replicate the gas phase dipole and quadrupole of these molecules (NIST 2006). Atomic charges for methane were taken from the Compass forcefield, which were specifically parameterized for methane. N₂ and H₂ atoms were assumed to be neutral. While a homonuclear diatomic N₂ does have a measured quadrupole moment, and thus some forcefields, such as the TraPPE forcefield (Potoff and Siepmann 2001) use a three site charge model with negative charges on the atoms and a balancing positive charge on the centre of mass. We have ignored electrostatic interactions on N₂ because firstly the Lennard-Jones param-

eters from the Compass forcefield assume no atomic charges, and secondly initial calculations with the charges from the TraPPE forcefield showed little change in the adsorption of N₂.

Because of the highly mobile nature of gases within the framework it is not practical to pre-calculate all the gas-gas interactions. Thus all dispersion/repulsion gas-gas interactions were calculated using pairwise Lennard-Jones summations, truncated at 18.5 Å by a cubic spline function. Electrostatic interactions were calculated with a shifted-force electrostatic potential (Fennell and Gezelter 2006). To ensure that this potential accurately represents the gas-gas electrostatic interactions within these systems some initial simulations were performed using both the shifted force potential and full Ewald summation. These simulations showed that there was little difference in adsorption between the two electrostatic representations. Since the shifted force potential is significantly faster this potential was used in the calculations.

To account for the flexibility of each gas molecule modification of the bond lengths and angles a gas internal coordinate change step was included with the usual addition, deletion, translation and rotation Monte Carlo steps. In this step an internal coordinate of the gas molecule is varied. The resulting change in energy is then modeled using the bond length and bond angle potentials in the Compass forcefield. Acceptance of this step is based on the total change in energy. All bond lengths and angles in each gas were varied in this fashion during the simulations.

Complete details of the forcefield parameters and gas charges can be found in the online resource.

2.4 Simulation

The adsorption of different gases was calculated using grand canonical Monte Carlo (GCMC) simulations. These were performed with our own code, Molasses. Addition, deletion, translation, rotation, regrowth and conformer steps were used within the grand canonical ensemble. In each simulation the framework unit cell was duplicated so that the simulation cell size was at least 37 Å in all directions, twice the potential cut-off. In each pressure step the simulation is started with an empty cell. The simulation cell was first equilibrated using 1×10^7 loading steps, and then ensemble averages were calculated over another 1×10^7 production steps. Corrections for the difference between the simulated absolute adsorption and experimentally measured ex-

cess adsorption were made by the method of Myers and Monson (2002). Gas fugacities were calculated using the Peng-Robinson equation of state (Peng and Robinson 1976).

3 Single gas loading

The loading of CO₂, H₂O, N₂, H₂ and CH₄ as a single gas at 298 K was calculated for COF-102, Cu₃(BTC)₂, MIL-47, MOF-5, MOF-74, MOF-177, Sc-MOF, ZIF-69 and Zn₂(BDC)₂(TED) over a pressure range of 0.5–15 bar. At room temperature each framework does not adsorb significant amounts of H₂. Indeed the concentration of H₂ in the void space in each framework did not exceed the concentration of gas in the surrounding reservoir. The other four gases do show significant adsorption within the framework. Figure 2 shows the simulated adsorption isotherms of CO₂,

Fig. 2 Loading of different gases in frameworks at 298 K

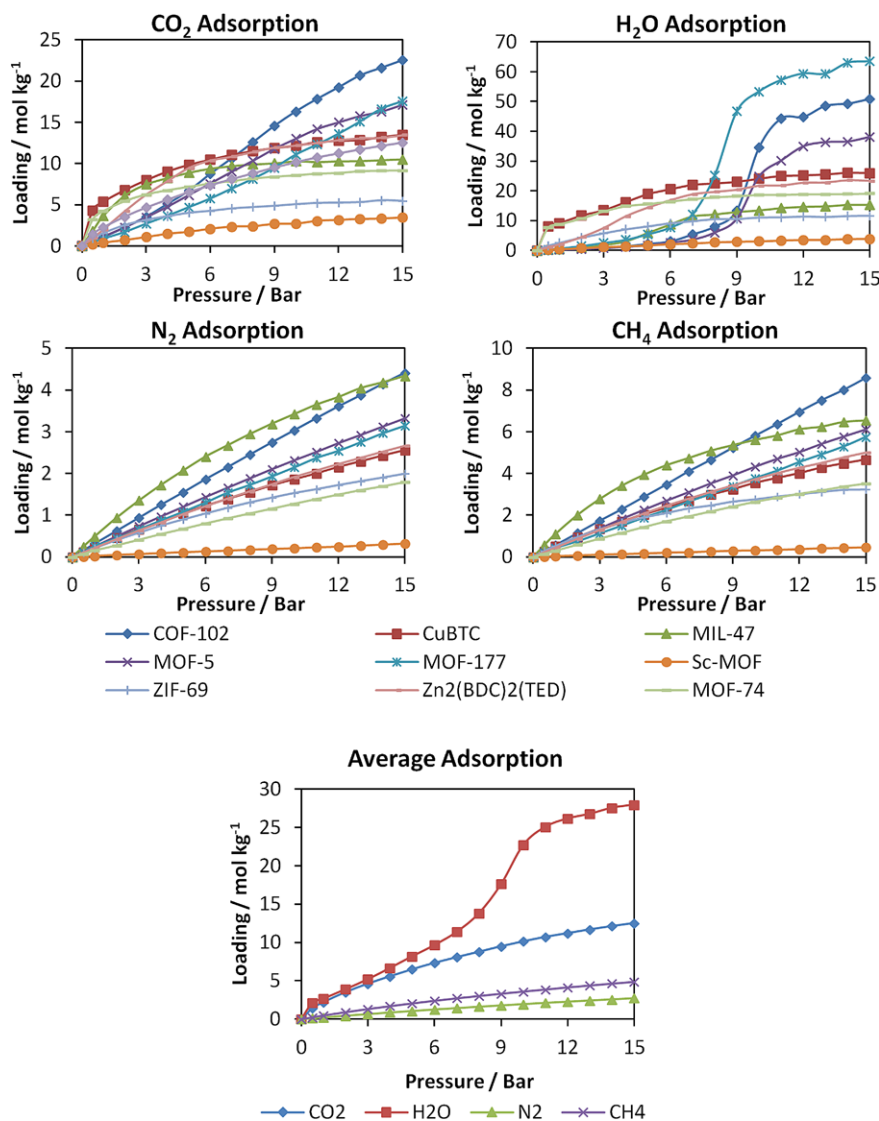
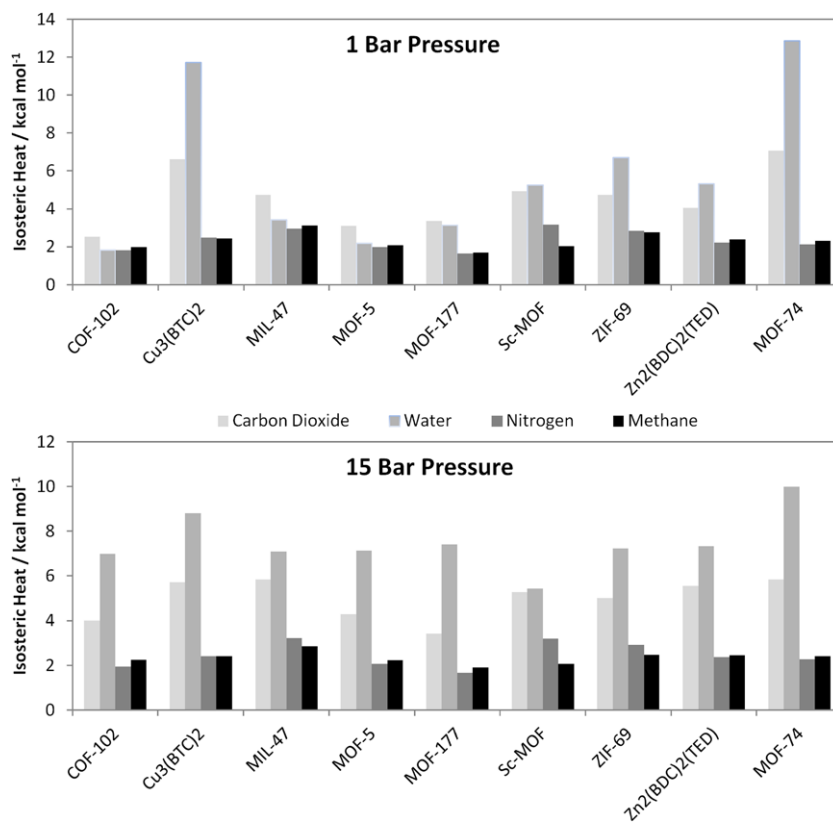


Fig. 3 Isothermic heats of adsorption at two different pressures



H₂O, N₂ and CH₄ in different frameworks, as well as the average loading across all the frameworks of each gas.

In terms of the separation of CO₂ from other gases this data shows that each framework is able to adsorb far more CO₂ than N₂ or CH₄. Generally each framework is also able to adsorb more H₂O than CO₂, especially at high pressure. Examining the isosteric heats of adsorption calculated for each gas and framework helps to clarify this. Figure 3 shows the calculated isosteric heats taken both at 1 bar and at 15 bar pressure. Here the isosteric heats of adsorption of N₂ and CH₄ are lower than those of both CO₂ and H₂O. This is easily rationalized by the non-polar nature of N₂ and CH₄, the dipolar and quadrupolar nature of H₂O and CO₂ respectively, and the highly polar nature of each framework. Because N₂ is a non-polar gas, it has much weaker interactions with the framework. Likewise H₂, which our simulations showed did not significantly adsorb into the framework at all, also has very weak interactions with the frameworks. Thus it should be expected that MOFs should be largely selective for polar gases over non-polar gases.

This can be more clearly seen in comparing the average positions of gas loading within the framework. In frameworks that have different polar and non-polar binding sites we observe that the gases bind preferentially at the different sites. Figure 4 shows the average centre of mass positions of CO₂, H₂O, N₂ and CH₄ at 1 bar in Cu₃(BTC)₂. Here CO₂ is shown in blue, H₂O in red, N₂ in green and CH₄ in yellow.

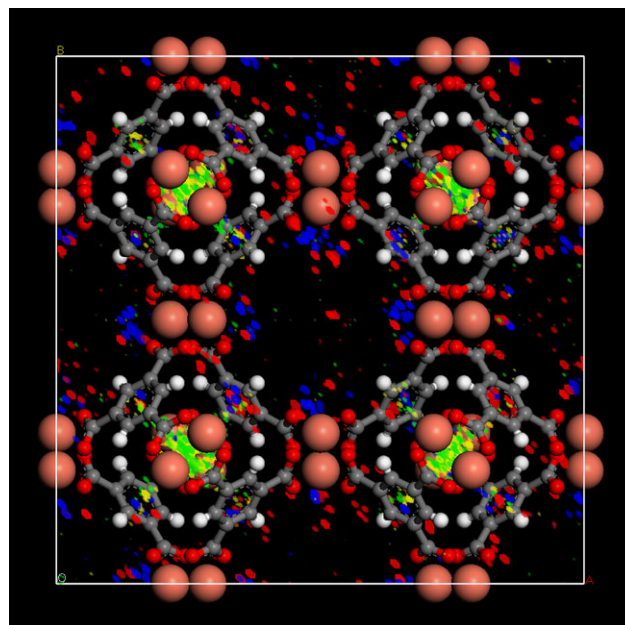


Fig. 4 (Color online) Average gas positions in Cu₃(BTC)₂ at 1 bar pressure and 298 K

This shows that the preferred adsorption sites for CO₂ and H₂O are in the large pores close to the copper atoms. This position maximizes the electrostatic interaction between the negatively charged oxygen and the positively charged cop-

per. In contrast N_2 and CH_4 , since they have no significant overall charge, concentrate in the small pores formed by the four aromatic rings. This maximizes the van der Waals interaction between gas and the framework. Since the different polar and non-polar gases have different mechanisms of adsorption, with the charge-based mechanism generally resulting in much more favorable adsorption energies, MOFs are generally selective for polar gases.

When comparing the adsorption of water and carbon dioxide the simulations clearly show that each framework has a higher maximum capacity for water adsorption than carbon dioxide. However looking at the adsorption energies reveals a much more complicated picture. As shown in Fig. 3 at low pressure H_2O has a similar heat of adsorption to CO_2 , which in most cases changes to a higher heat of adsorption at high pressure. This demonstrates that while the gas-framework interactions for both gases are similar, the gas-gas interactions in water are higher. Thus when some H_2O adsorbs onto the surface this increases the capacity of the framework for binding further water molecules. A similar adsorption mechanism is $Cu_3(BTC)_2$ has been proposed by Snurr and co-workers for the adsorption of CO_2 in the presence of H_2O (Yazaydin et al. 2009). The only cases for which this is not so are in the MOFs $Cu_3(BTC)_2$ and MOF-74, both of which feature unsaturated metal cations. These cations form low energy binding sites that have more favorable interactions than bound water molecules. Thus when these sites are populated the overall heat of adsorption is reduced.

Directly comparing the water and carbon dioxide gas-framework interaction energies also helps to illustrate the differences between the gas-frame and gas-gas interactions at different temperatures. Figure 5 shows the ratio of CO_2 to H_2O gas-framework binding energies at 1 and 15 bars, as well as the CO_2 to H_2O adsorbances at 1 and 15 bars. This

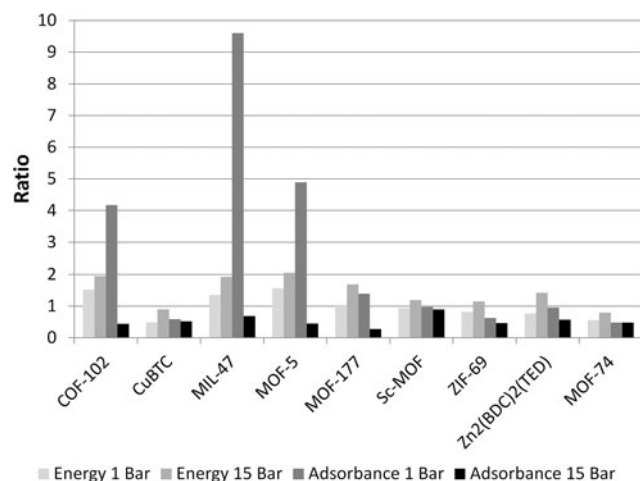


Fig. 5 Ratios of CO_2 to H_2O gas-framework interaction energies and adsorbances

data reveals that at low pressures there is some correlation between the ratio of the framework energies and the adsorbances of CO_2 and H_2O . Those frameworks that have higher interaction energies with CO_2 than H_2O also have a higher adsorbance. This correlation is destroyed at high pressure, where the gas-gas interactions become more important. At higher pressures it is therefore not simple to predict the loading of CO_2 and H_2O . Since the gas-gas interactions for each adsorbent are significant, the specific mixing properties of the gases within the pore space become important in determining loading.

4 PSA and VSA simulations

The previously observed shifting preference in gas-framework and gas-gas interactions makes adsorptive selectivity difficult to determine. Ultimately the selectivity is found by balancing this inherent framework interaction selectivity with the different interactions of the gases with each other and also their ability to mix within the specific pore space of the framework. GCMC simulations, where the surrounding gas reservoir contains a mixture of gases, are able to balance these different factors. The main problem with these simulations is that the results are difficult to generalize. Thus to gain a full picture of the adsorption of different gases into a framework the whole gas mixture variable space needs to be scanned with different simulations. In these cases where a full understanding of different gas mixtures is required more approximate methods, such as Ideal Adsorbed Solution Theory (IAST) have been shown to be effective for more ideal gases (Liu and Smit 2009a). However for the simulation of specific either non-ideal gas mixtures or adsorbents as found in various engineering problems direct GCMC simulations provide more reliable data (Chen and Sholl 2007).

Since we are interested in the application of MOFs as separators of CO_2 from flue gas we have performed simulations targeted towards this application. In one series of simulations we have modeled a typical VSA post combustion CO_2 separation process and in another a typical PSA pre-combustion process. Since post-combustion flue gas is typically at atmospheric pressure it is usually considered most suitable for VSA separation. Here we assume a gas mixture of 15% CO_2 , 15% H_2O and 70% N_2 for the post combustion gas stream. Likewise, since many coal gasification processes involve pressurizing the product gas pre-combustion separation is best done using PSA. Here we assume a gas mixture of 25% CO_2 , 12% H_2O , 23% N_2 and 40% H_2 for the pre-combustion gas stream.

In pressure swing adsorption, the difference in adsorption between the upper and lower pressures, rather than the absolute adsorption, is the critical factor. This represents the

amount of gas adsorbed and desorbed in each cycle. Thus the selectivity of each framework has been calculated based on this working capacity. The VSA working capacity is calculated between 0.1 and 1 bar, whereas the PSA working capacity is calculated between 1 and 15 bars. To illustrate the effects of temperature simulations were run at two different temperatures. To allow for the specific water content, VSA simulations were run at 328 and 373 K, while the PSA simulations were run at 393 and 473 K.

A summary of these simulations, specifically the CO₂ working capacity of each framework and the selectivity for CO₂ from N₂ and H₂O, are shown in Fig. 6 and 7.

From this data a number of conclusions can be made. First in each process it can be seen that the tested frameworks are generally selective for carbon dioxide over nitrogen. This is due in large part to the larger heat of adsorption of CO₂ and the larger electrostatic interactions between CO₂ and the framework. This can be seen in a number of ways. Firstly the more polar frameworks, namely Cu₃(BTC)₂ and MOF-74 both have good selectivity of CO₂ over N₂. Sc-MOF has large selectivity because the small pores in the framework do not allow the formation of adsorbed gas layers, and the binding energy of CO₂ and H₂O onto the surface of the pore is much lower. The general importance of adsorption energy differences in selectivity is also seen in the

effects of temperature on selectivity. In every case selectivity is reduced at higher temperature, as at higher temperatures differences in adsorption energy becomes less significant.

The picture revealed for adsorption of CO₂ over water is more complicated. In this case not only are adsorption energies onto the framework important, but the interaction energy of water molecules themselves becomes im-

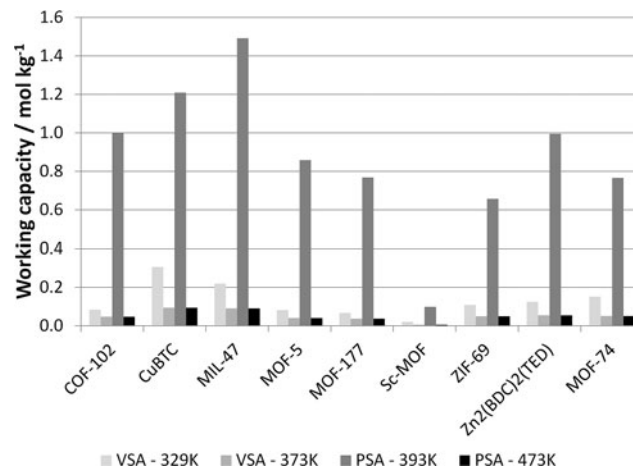
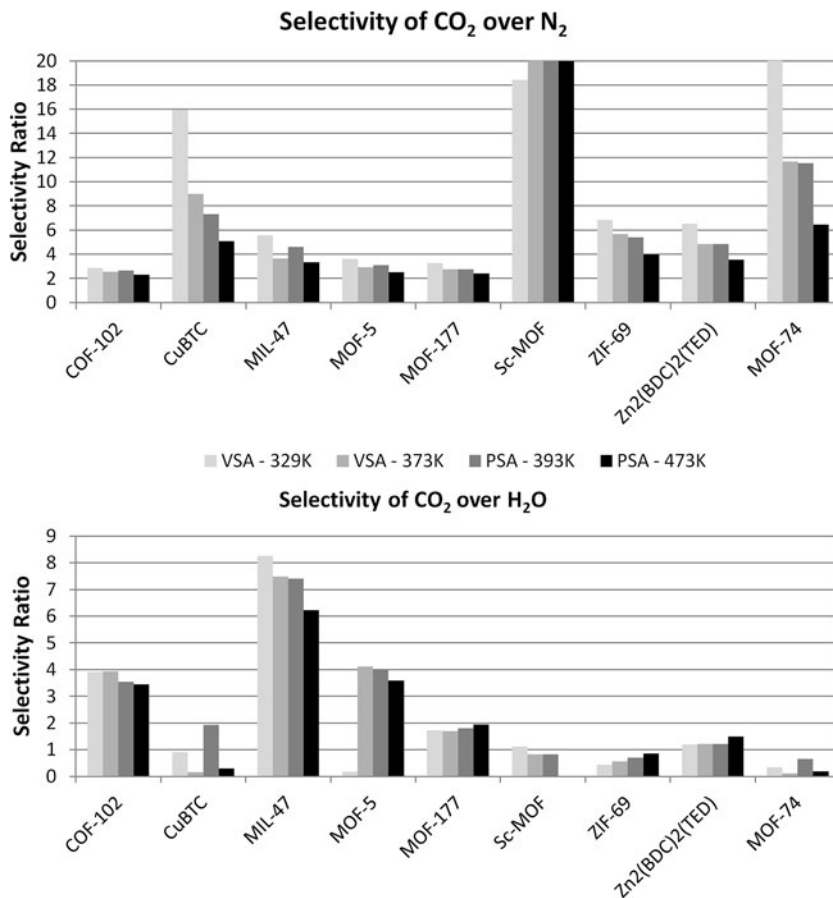


Fig. 6 Total CO₂ loading in the relevant working capacity

Fig. 7 Selectivities for CO₂ adsorption in different MOFs



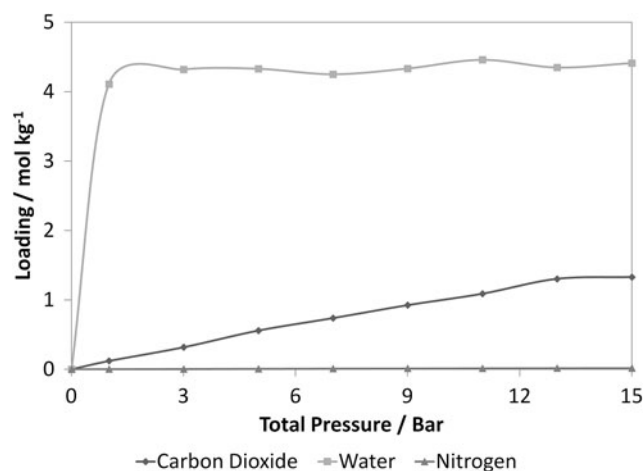


Fig. 8 Adsorption isotherms in a PSA simulation in $\text{Cu}_3(\text{BTC})_2$ at 393 K

portant. This leads to a number of different possible adsorption mechanisms. Some frameworks, such as the polar $\text{Cu}_3(\text{BTC})_2$ and MOF-74 have a higher adsorption energy for H_2O than CO_2 , and thus are more selective for H_2O than CO_2 . Here the feature that leads to large selectivity of CO_2 over N_2 also leads to low selectivity of CO_2 over H_2O .

In some simulations the polar frameworks show selective adsorption of CO_2 over the pressure range of the adsorption method. One example is in the PSA simulation at 393 K in $\text{Cu}_3(\text{BTC})_2$. The adsorption isotherms of CO_2 , H_2O and N_2 in this process are shown in Fig. 8. In this case the framework is close to saturated with water at the low pressure point. Thus as the pressure is increased the framework is unable to adsorb more water. Therefore while the framework does in total adsorb a lot of water it adsorbs little during the pressure swing, and therefore the framework becomes selective for CO_2 during the adsorption pressure swing.

In contrast to this other more non-polar frameworks, such as COF-102 show reasonable selectivity for CO_2 over H_2O . Here the gas-framework interactions consist mostly of dispersion interactions, which favour the adsorption of CO_2 . Water adsorption is therefore low because it is not selectively adsorbed by the framework, and in these conditions not enough water is adsorbed to start condensing in the pore. This effect is most dramatically seen in the simulations of MOF-5. Here at low temperature the framework is selective for H_2O , while at higher temperatures it becomes selective for CO_2 . At low temperature enough H_2O is adsorbed to form selective sites for further H_2O adsorption, and so the framework becomes loaded with a lot of water. At higher temperature, since there is overall less gas adsorbed, the water adsorption drops below the critical level for this to happen, providing space for much more CO_2 to adsorb.

One of the most interesting gas selection mechanisms occurs in MIL-47. In high humidity and ambient temperature, MIL-47 is able to adsorb 1.5 times more H_2O than CO_2 ,

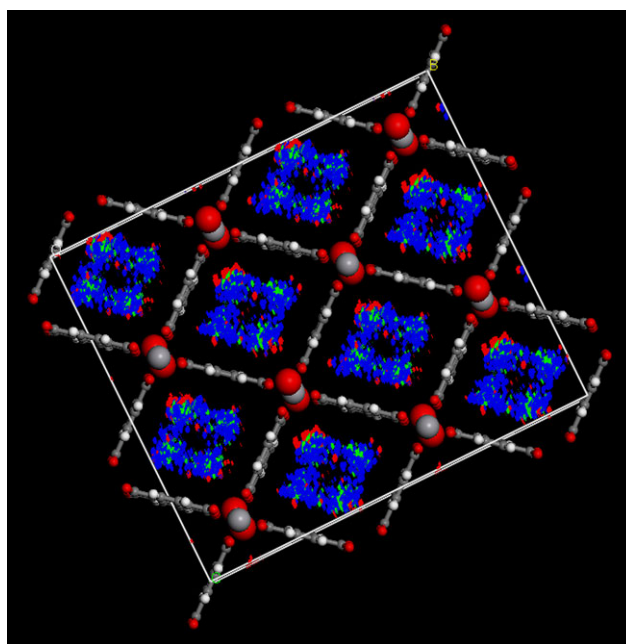


Fig. 9 (Color online) Average positions of CO_2 , H_2O and N_2 in MIL-47, taken from the VSA simulation at 1 bar pressure and 328 K

yet at low humidity it has a low uptake of H_2O . This indicates that the framework is hydrophobic and relies on the condensation of water in the pores to achieve large water adsorption. In each mixed gas simulation the amount of water in the gas mixture was too low for condensation in the pores to occur, and thus MIL-47 is selective for CO_2 over H_2O .

The reasons for the hydrophobicity of the framework and the large selectivity over water can be seen in the average positions of gas binding. Figure 9 shows the average center of mass positions of CO_2 (blue), H_2O (red) and N_2 (green) in MIL-47. The pores in MIL-47 have a rhombus shape, with the polar metal and oxygen atoms at each corner. These corners in the channel represent the lowest energy binding sites. Here each gas molecule is able to maximize their dispersion interaction and also interact with the highly charged metal cations. CO_2 and N_2 , both being linear, are able to adsorb into any of the four corners. H_2O , not being linear, is geometrically constrained to only adsorbing onto the large angle corner. The adsorption of CO_2 and N_2 into the small angle corner prevents the condensation of water in the channel, thus limits the amount of H_2O adsorbed at low pressures. This has the effect of making MIL-47 selective against H_2O .

In terms of the amount of CO_2 adsorbed in each process the PSA process at 393 K by far adsorbs the most CO_2 . At 473 K the temperature is too high to allow significant adsorption of CO_2 . In the VSA process, even though they are at lower temperature, the total pressure is not sufficient to allow significant CO_2 adsorption. The percentage of CO_2 in the gas in the VSA simulations is also lower than that in the PSA simulations. Total CO_2 adsorbed in the VSA processes

could be increased by using frameworks that have large low pressure uptake of CO₂. One such class of frameworks with this property is the ZMOFs (Zeolitic MOFs) such as rho-ZMOF (Babarao et al. 2009). This framework shows excellent selectivity of CO₂ from N₂, but given the highly polar nature of the framework selectivity CO₂ from H₂O may be problematic. With these frameworks however the PSA method has a far larger adsorption of CO₂ in the operative pressure range. This suggests that MOFs are more suitable for use as adsorbents in PSA separations of pre-combustion gas mixtures than for VSA separations of post combustion mixtures.

5 Conclusions

Using GCMC calculations the adsorption, both of pure gases and mixtures of CO₂, H₂O, N₂, CH₄ and H₂ have been simulated. From these simulations several conclusions about the CO₂ gas separation properties of these frameworks were made. H₂ is only sparingly adsorbed in the frameworks at the separation temperatures considered; thus the frameworks are highly selective for CO₂ over H₂. N₂ and CH₄ adsorb into the frameworks with a lower isosteric heat than more polar gases, and thus all the tested frameworks were selective for CO₂ over N₂. Reducing the temperature was found to increase this selectivity. The competitive adsorption of CO₂ over water is more complicated, dependant on the balance between gas-gas and gas-framework interactions rather than differences in isosteric heat of adsorption. Less polar frameworks as well as access to binding sites (as determined by the fine details of the specific pore geometry) were shown to increase the adsorptive selectivity of CO₂ over H₂O. Increasing the temperature can increase the selectivity of the framework, as it can retard water condensation on the pore surface.

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References

- Aaron, D., Tsouris, C.: Separation of CO₂ from flue gas: a review. *Sep. Sci. Technol.* **40**, 321–348 (2005)
- Babarao, R., Jiang, J.: Molecular screening of metal organic frameworks for CO₂ storage. *Langmuir* **24**, 6270–6278 (2008)
- Babarao, R., Jiang, J.: Unprecedentedly high selective adsorption of gas mixtures in rho zeolite-like metal-organic framework: a molecular simulation study. *J. Am. Chem. Soc.* **131**, 11417–11425 (2009)
- Babarao, R., Jiang, J., Sandler, S.I.: Molecular simulations for adsorptive separation of CO₂/CH₄ mixture in metal-exposed, catenated, and charged metal organic frameworks. *Langmuir* **25**, 5239–5247 (2009)
- Bae, Y.-S., Mulfort, K.L., Frost, H., Ryan, P., Punathanam, S., Broadbelt, L.J., Hupp, J.T., Snurr, R.Q.: Separation of CO₂ from CH₄ using mixed-ligand metal organic frameworks. *Langmuir* **24**, 8592–8598 (2008)
- Banerjee, R., Phan, A., Wang, B., Knobler, C., Furukawa, H., O’Keeffe, M., Yaghi, O.M.: High-throughput synthesis of zeolitic imidazolate frameworks and application to CO₂ capture. *Science* **319**, 939–943 (2008)
- Barthelet, K., Marrot, J., Riou, D., Férey, G.: A breathing hybrid organic-inorganic solid with very large pores and high magnetic characteristics. *Angew. Chem. Int. Ed.* **41**, 281–284 (2002)
- Chae, H.K., Siberio-Perez, D.Y., Kim, J., Go, Y., Eddaoudi, M., Matzger, A.J., O’Keeffe, M., Yaghi, O.M.: A route to high surface area, porosity and inclusion of large molecules in crystals. *Nature* **427**, 523–527 (2004)
- Chen, H., Sholl, D.S.: Examining the accuracy of ideal adsorbed solution theory without curve-fitting using transition matrix Monte Carlo simulations. *Langmuir* **23**, 6431–6437 (2007)
- Cheng, Y., Kondo, A., Noguchi, H., Kajiro, H., Urita, K., Ohba, T., Kaneko, K., Kanoh, H.: Reversible structural change of Cu-MOF on exposure to water and its CO₂ adsorptivity. *Langmuir* **25**, 4510–4513 (2009)
- Chui, S.S.Y., Lo, S.M.F., Charmant, J.P.H., Orpen, A.G., Williams, I.D.: A chemically functionalizable nanoporous material [Cu₃(TMA)₂(H₂O)₃]_n. *Science* **283**, 1148–1150 (1999)
- Dybtssev, D.N., Chun, H., Kim, K.: Rigid and flexible: a highly porous metal-organic framework with unusual guest-dependent dynamic behavior. *Angew. Chem. Int. Ed.* **43**, 5033–5036 (2004)
- Fennell, C.J., Gezelter, J.D.: Is the Ewald summation still necessary? Pairwise alternatives to the accepted standard for long-range electrostatics. *J. Chem. Phys.* **124**, 234104-12 (2006)
- Frenkel, D., Smit, B.: Monte Carlo simulations. In: *Understanding Molecular Simulation*, pp. 23–61. Academic Press, San Diego (2002a)
- Frenkel, D., Smit, B.: Monte Carlo simulations in various ensembles. In: *Understanding Molecular Simulation*, pp. 111–137. Academic Press, San Diego (2002b)
- Greathouse, J.A., Allendorf, M.D.: The interaction of water with MOF-5 simulated by molecular dynamics. *J. Am. Chem. Soc.* **128**, 10678–10679 (2006)
- Jose, M.S., Emilio, A., Julian, D.G., Alberto, G., Javier, J., Pablo, O., Daniel, S.-P.: The SIESTA method for ab initio order-*N* materials simulation. *J. Phys. Condens. Matter.* **2745** (2002)
- Keskin, S., Liu, J., Rankin, R.B., Johnson, J.K., Sholl, D.S.: Progress, opportunities, and challenges for applying atomically detailed modeling to molecular adsorption and transport in metal organic framework materials. *Ind. Eng. Chem. Res.* **48**, 2355–2371 (2009)
- Klontzas, E., Tyljanakis, E., Froudakis, G.E.: Designing 3D COFs with enhanced hydrogen storage capacity. *Nano Lett.* **10**, 452–454 (2010)
- Konduru, N., Lindner, P., Assaf-Anid, N.M.: Curbing the greenhouse effect by carbon dioxide adsorption with zeolite 13X. *AIChE J.* **53**, 3137–3143 (2007)
- Li, H., Eddaoudi, M., O’Keeffe, M., Yaghi, O.M.: Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* **402**, 276–279 (1999)
- Li, J.-R., Kuppler, R.J., Zhou, H.-C.: Selective gas adsorption and separation in metal-organic frameworks. *Chem. Soc. Rev.* **38**, 1477–1504 (2009)
- Li, Y., Yang, R.T.: Gas adsorption and storage in metal-organic framework MOF-177. *Langmuir* **23**, 12937–12944 (2007)
- Liang, Z., Marshall, M., Chaffee, A.L.: CO₂ adsorption-based separation by metal organic framework (Cu-BTC) versus zeolite (13X). *Energy Fuels* **23**, 2785–2789 (2009)

- Liu, B., Smit, B.: Comparative molecular simulation study of CO₂/N₂ and CH₄/N₂ separation in zeolites and metal organic frameworks. *Langmuir* **25**, 5918–5926 (2009a)
- Liu, D., Zheng, C., Yang, Q., Zhong, C.: Understanding the adsorption and diffusion of carbon dioxide in zeolitic imidazolate frameworks: a molecular simulation study. *J. Phys. Chem. C* **113**, 5004–5009 (2009b)
- Martin-Calvo, A., Garcia-Perez, E., Castillo, J.M., Calero, S.: Molecular simulations for adsorption and separation of natural gas in IRMOF-1 and Cu-BTC metal-organic frameworks. *Phys. Chem. Chem. Phys.* **10**, 7085–7091 (2008)
- Mayo, S.L., Olafson, B.D., Goddard, W.A.: DREIDING: a generic force field for molecular simulations. *J. Phys. Chem.* **94**, 8897–8909 (2002)
- Miller, S.R., Wright, P.A., Devic, T., Serre, C., Férey, G., Llewellyn, P.L., Denoyel, R., Gaberova, L., Filinchuk, Y.: Single crystal X-ray diffraction studies of carbon dioxide and fuel-related gases adsorbed on the small pore scandium terephthalate metal organic framework, Sc₂(O₂CC₆H₄CO₂)₃. *Langmuir* **25**, 3618–3626 (2009)
- Millward, A.R., Yaghi, O.M.: Metal organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature. *J. Am. Chem. Soc.* **127**, 17998–17999 (2005)
- Morton, A.: First climate refugees start move to new island home. *The Age* (2009)
- Myers, A.L., Monson, P.A.: Adsorption in porous materials at high pressure: theory and experiment. *Langmuir* **18**, 10261–10273 (2002)
- NIST: Computational chemistry comparison and benchmark database. <http://srdata.nist.gov/cccbdb> (2006). Accessed 13th May 2010
- Peng, D.-Y., Robinson, D.B.: A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **15**, 59–64 (1976)
- Potoff, J.J., Siepmann, J.I.: Vapor-liquid equilibria of mixtures containing alkanes, carbon dioxide, and nitrogen. *AIChE J.* **47**, 1676–1682 (2001)
- Ramsahye, N., Maurin, G., Bourrelly, S., Llewellyn, P., Devic, T., Serre, C., Loiseau, T., Férey, G.: Adsorption of CO₂ in metal organic frameworks of different metal centres: grand canonical Monte Carlo simulations compared to experiments. *Adsorption* **13**, 461–467 (2007a)
- Ramsahye, N.A., Maurin, G., Bourrelly, S., Llewellyn, P.L., Loiseau, T., Serre, C., Férey, G.: On the breathing effect of a metal-organic framework upon CO₂ adsorption: Monte Carlo compared to microcalorimetry experiments. *Chem. Commun.* 3261–3263 (2007b) (Cambridge, UK)
- Rappe, A.K., Casewit, C.J., Colwell, K.S., Goddard, W.A., Skiff, W.M.: UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. *J. Am. Chem. Soc.* **114**, 10024–10035 (2002)
- Rosseinsky, M.J.: Recent developments in metal-organic framework chemistry: design, discovery, permanent porosity and flexibility. *Microporous Mesoporous Mater.* **73**, 15–30 (2004)
- Sun, H.: COMPASS: an ab initio force-field optimized for condensed-phase applications overview with details on alkane and benzene compounds. *J. Phys. Chem. B* **102**, 7338–7364 (1998)
- Wax, E.: In flood-prone Bangladesh, a future that floats. *The Washington Post* (2007)
- Wells, B., Chaffee, A.: Advances in simulating gas adsorption in metal-organic and covalent-organic frameworks for the rational design of selective CO₂ adsorbing materials (in preparation)
- Wells, B.A., Liang, Z., Marshall, M., Chaffee, A.L.: Modeling gas adsorption in metal organic frameworks. *Energy Procedia* **1**, 1273–1280 (2009)
- Yaghi, O.M., O’Keeffe, M., Ockwig, N.W., Chae, H.K., Eddaoudi, M., Kim, J.: Reticular synthesis and the design of new materials. *Nature* **423**, 705–714 (2003)
- Yang, Q., Zhong, C.: Molecular simulation of carbon dioxide/methane/hydrogen mixture adsorption in metal organic frameworks. *J. Phys. Chem. B* **110**, 17776–17783 (2006a)
- Yang, Q., Xue, C., Zhong, C., Chen, J.-F.: Molecular simulation of separation of CO₂ from flue gases in Cu-BTC metal-organic framework. *AIChE J.* **53**, 2832–2840 (2007)
- Yang, Q., Zhong, C., Chen, J.-F.: Computational study of CO₂ storage in metal organic frameworks. *J. Phys. Chem. C* **112**, 1562–1569 (2008)
- Yazaydin, A.O., Benin, A.I., Faheem, S.A., Jakubczak, P., Low, J.J., Willis, R.R., Snurr, R.Q.: Enhanced CO₂ adsorption in metal-organic frameworks via occupation of open-metal sites by coordinated water molecules. *Chem. Mater.* **21**, 1425–1430 (2009)